

PROPERTIES AND POTENTIAL ENVIRONMENTAL APPLICATIONS OF CARBON ADSORBENTS FROM WASTE TIRE RUBBER

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KEYWORDS: carbon adsorbent, pyrolysis, tire recycling, air pollution

ABSTRACT

The properties of tire-derived carbon adsorbents (TDCA) produced from select tire chars were compared with those derived from an Illinois coal and pistachio nut shells. Chemical analyses of the TDCA indicated that these materials contain metallic elements not present in coal- and nut shell-derived carbons. These metals, introduced during the production of tire rubber, potentially catalyze steam gasification reactions of tire char. TDCA carbons contained larger meso- and macropore volumes than their counterparts derived from coal and nut shell (on the moisture- and ash-free-basis). Adsorptive properties of the tire-derived adsorbent carbons for air separation, gas storage, and gas clean up were also evaluated and compared with those of the coal- and nut shell derived carbons as well as a commercial activated carbon. The results revealed that TDCA carbons are suitable adsorbents for removing vapor-phase mercury from combustion flue gases and hazardous organic compounds from industrial gas streams.

INTRODUCTION

The issue of disposing of waste tires in industrialized nations has become a pervasive issue that requires remedy. Data from a U.S. EPA study in 1993 indicates that 242 million waste tires are generated in the United States each year, corresponding to approximately one tire per US citizen per year¹. The trend of one tire generated per person-year is generally applicable to industrialized nations. Tire stockpiles have created significant environmental concerns: the open shape of tires allows rainwater to collect, making them ideal breeding grounds for mosquitoes and vermin; tire stockpile fires are of concern since used tires are readily combustible and are difficult to extinguish; and finally, tire stockpiles are an aesthetic concern, since they are frequently located near densely-populated areas where large numbers of tires are generated. The millions of metric tonnes of waste tires are a potential feedstock for the production of new materials. However, data from the U.S. EPA indicates that only ~20% of waste tires are utilized in a given year, and the rest are disposed of in tire stockpiles or landfills; two to three billion tires were stored thusly as of 1993¹.

Pyrolysis has been proposed as a method for decomposing some of the tire rubber to salable oil, gas, and char (principally carbon black). The yield of char from tire pyrolysis is about 30 wt%, which could be upgraded into a value-added tire-derived carbon adsorbent (TDCA). Producing TDCA from waste tires may potentially provide an economic incentive for commercializing tire pyrolysis as a recycling process.

The work presented in this paper summarizes the results from an ongoing collaborative research program between the Illinois State Geological Survey and the University of Illinois at Urbana-Champaign to prepare and evaluate the applications of TDCA for gas purification and clean up. TDCA samples were prepared in both laboratory- and pilot-scale reactors. The properties of TDCA samples were compared to those derived from a high-sulfur bituminous Illinois coal and pistachio nut shells. These adsorbents were evaluated for removal of vapor-phase mercury species (Hg^0 and $HgCl_2$) from simulated coal combustion flue gases and for capture of gaseous organic solvents, including acetone and methyl-ethyl-ketone (MEK). These compounds are of concern due to their large source strength to the atmosphere (Table 1).

Adsorption processes are widely utilized in air pollution control operations for removing hazardous gases from industrial flue gas streams. A porous solid with large surface area and micropore volume is key for efficient removal of pollutants in any adsorption process. Adsorbents produced from different precursor materials will have differing properties due to inherent variations in the chemical and physical nature of precursor materials.

METHODOLOGY

Carbon adsorbents were prepared by heating the tire, coal, or pistachio shell in a fixed-bed reactor to 850°C under a nitrogen purge. The char was then activated in steam at 850°C. Activation rates of the precursor chars were obtained with a thermogravimetric analyzer (CAHN TG-131) in either a 100% CO₂ or (50% CO₂)/(50% steam) mixture at 850°C. The precursors were analyzed for their moisture, ash, carbon, hydrogen, nitrogen, and total sulfur contents using standard ASTM methodology (Table 2).

The surface structure and morphology of prepared adsorbents were evaluated via nitrogen adsorption (at 77 K) and scanning electron microscopy. Nitrogen adsorption isotherms were determined via an adsorption apparatus (Micromeritics ASAP 2400). Surface areas were determined via the standard BET equation. Total pore volumes were determined at $P/P_0=0.98$ and micropore volumes were evaluated using the 3-D pore size distribution model developed at ISGS/UIUC.³ Scanning electron micrographs (SEM) were collected from prepared samples (Amary 1830).

Elemental mercury (Hg⁰) and mercuric chloride (HgCl₂) equilibrium adsorption capacities for prepared samples were completed by Radian International LLC (Austin, TX). Tests were carried out in a simulated flue gas containing 1600 ppm, SO₂, 50 ppm, HCl, 12% CO₂, 7% H₂O, 6% O₂, and 40-60 µg/N-m³ Hg⁰ or HgCl₂. Adsorption capacities were measured using cold-vapor atomic adsorption. Equilibrium acetone and MEK capacities were determined in a gravimetric analyzer (CAHN 2000) using standardized gas cylinders diluted with nitrogen.

RESULTS AND DISCUSSION

Proximate analyses of the adsorbent precursor materials indicate that the principle differences are in the ash, sulfur, and carbon contents (Table 2). The ash content of pistachio shells is negligible in comparison with coal and tire-based materials. Ash contents are of interest since concentrations of trace species, especially metals, likely influence gasification rates and adsorption properties of materials. Total sulfur contents of precursor adsorbents also differed, again with pistachio having a negligible sulfur content in comparison to the coal and tire precursors. Sulfur contents are of interest, since they likely influence the adsorption of mercury species.

The steam gasification rate (on the total mass basis) of tire char was larger than the coal char (Figure 1). Its CO₂ gasification rate was, however, much smaller than the pistachio char. Properties of select carbon adsorbents prepared in the fixed-bed reactor are presented in Table 3. The data are shown for test conditions that resulted in about 15% yield in adsorbent prepared from tire and pistachio shell, and about 30% yield from the coal. The surface area of the TDCA (389 m²/g) was about one-half of the coal and pistachio carbons. The TDCA, however, had 32% larger total pore volume (0.670 vs 0.505 cc/g) than the coal and pistachio carbons. Pistachio and coal carbons were more microporous than TDCA; more than 50% of the pores in the coal and pistachio carbons were in the micropore range as compared to 34% for the TDCA. TDCAs with surface areas as large as 1000 m²/g, and micropore volumes as large as 0.5 cc/g have been prepared (Figure 2). The reactivity and pore structure data suggest that there should not be any difficulties in developing porosity in tire-derived char using steam.

Scanning electron micrographs of the pistachio-derived carbon revealed that it had a more heterogenous and "rougher" surface than coal-derived carbon (Figures 3 and 5). The surface texture of the TDCA was intermediate between the coal and the pistachio-derived carbons (Figure 4) with various rod-like and clusters of matters present on its surface. EDS revealed that the rod-like matters were typically composed of zinc and sulfur species, and that the jagged "globes" were generally composed of calcium and Si. It appears that ZnO (an additive added to tire) is converted to ZnS during the activation of tire char with steam.

Air pollution applications of adsorbents. Coal-derived carbon had the largest capacity (2718 µg/g) for adsorption of Hg⁰ from the simulated coal combustion flue gas followed by tire- (872 µg/g) and pistachio-derived (500 µg/g) carbons (Figure 6). The TDCA and pistachio carbon, however, had about five times larger capacity for adsorption of HgCl₂ than their coal-derived counterpart. The presence of larger micropore volume and larger concentration of organic sulfur in the coal-derived carbon was potentially responsible for the large Hg adsorption capacity of this sample.⁴ Since tire rubber contains organically bound sulfur from the vulcanization process, it could potentially be a suitable precursor for preparing effective Hg adsorbent. Indeed, the results from extensive mercury testing with several TDCAs, using five different compositions of simulated coal combustion flue gas, revealed that TDCA is an effective sorbent for removal of both Hg and HgCl₂.⁵

Plots of capacity of TDCA for adsorption of acetone and MEK as a function of the adsorbate concentration (ppm_i) at select temperatures are shown in Figure 7. As expected, the adsorption capacity increased with increasing adsorbate concentration, and decreased with increasing temperature. In the case of acetone, the adsorption capacity ranged from 15 to 41 mg/g to 59 to 125 mg/g as temperature varied from 20°C to 50°C. For MEK, the adsorption capacity ranged from 43

to 101 mg/g to 93 to 197 mg/g as temperature varied from 20°C to 50°C. The adsorption of MEK was larger than the adsorption of acetone at the same conditions of temperature and adsorbate concentration. Equilibrium adsorption capacities for acetone were also determined for a commercial carbon (Calgon BPL, surface area = 965 m²/g) in a previous study.⁶ The equilibrium acetone capacities for TDCA was about 70% of the capacity observed for BPL, 225 mg/g at 10000 ppm.

CONCLUSIONS

The work presented here showed that carbon adsorbents with adequate surface area and pore volume could be prepared from waste tire rubber. Furthermore, adsorption studies indicated that TDCAs were suitable sorbents for removal of trace amounts of vapor-phase mercury from coal combustion flue gases, and for purification of gas streams containing hazardous organic compounds. Further work is required to identify the potential application of TDCA for other pollution control operations. In addition, research in identifying the roles of various metals in the waste tire during thermal processing, pore structure development, and any catalytic properties during adsorption/desorption processes should be investigated. Finally, the commercial success for producing TDCA depends on the market size and the selling price for both the tire-derived oil and the TDCA.

ACKNOWLEDGMENTS

Support from the Office of Solid Waste Research at the University of Illinois at Urbana-Champaign made this research possible.

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Table 1. Total air emissions (million kg per year), 1988-1998.

	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998
MEK	64.3	63.9	61.2	49.6	42.5	39.4	36.4	31.9	27.4	24.2	21.1
acetone	96.5	96.2	88.5	74.3	63.4	59.0	---	---	---	---	---
mercury	0.010	0.011	0.010	0.008	0.006	0.005	0.005	0.006	0.006	0.006	0.006

Source: U.S. EPA (<http://www.epa.gov/triexplorer/trends.htm>)

Note: Acetone removed from TRI in 1994

Table 2. Properties of raw sorbent materials.

	coal	raw tire	tire char	pistachio shell
moisture	9.3	0.5	0.3	4.4
ash ^a	11.5	3.0	15.4	0.2
carbon ^a	68.1	87.2	78.8	48.0
hydrogen ^a	4.8	7.6	0.8	6.1
nitrogen ^a	1.2	0.2	0.2	0.1
oxygen ^{a,b}	10.5	0.9	2.0	45.5
total sulfur ^a	3.7	1.6	2.9	0.2

^a moisture-free values

^b oxygen content determined by difference

Table 3. Properties of prepared adsorbents.

	coal	tire	pistachio shell
ash [wt. %]	27.0	---	---
sulfur content	1.6	---	---
yield [%]	30.0	14.7	14.8
surface area [m ² /g]	787	389	775
total pore volume [cc/g]	0.504	0.670	0.505
micropore volume [cc/g]	0.265	0.230	0.312

--- = not measured

Figure 1. Gasification rate of select precursor materials in CO₂ or steam/CO₂ mixture at 850°C.

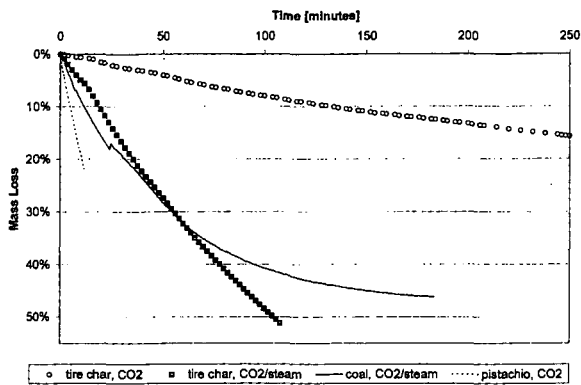


Figure 2. (A) BET-N₂ surface area and (B) micropore volume vs. yield for TDCA.

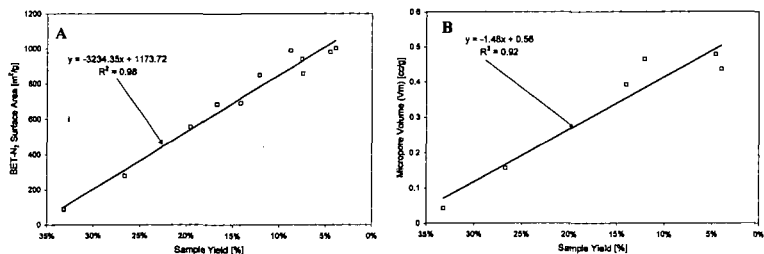


Figure 3. SEM of Illinois coal-derived adsorbent (4780x magnification).

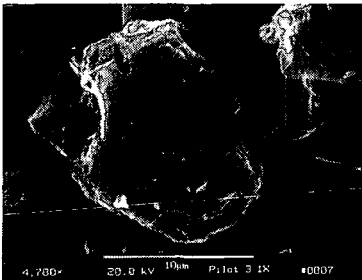


Figure 4. SEM of tire-derived adsorbent (3800x magnification).

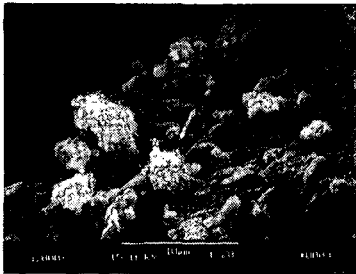


Figure 5. SEM of pistachio shell-derived adsorbent (3800x magnification).

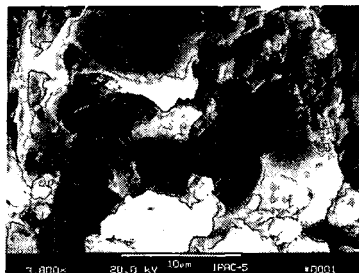


Figure 6. Hg^0 and HgCl_2 equilibrium capacities of adsorbents at 135°C.

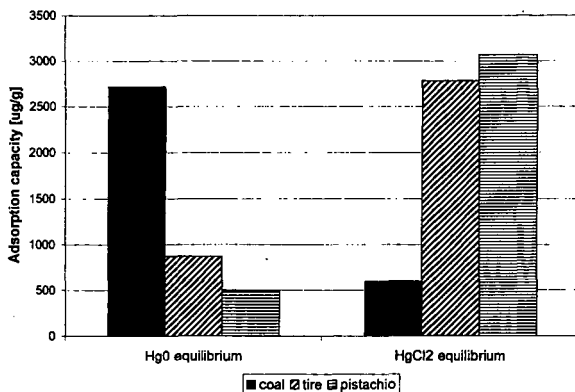


Figure 7. (A) Acetone and (B) MEK capacities of TDCA at 20-50°C.

